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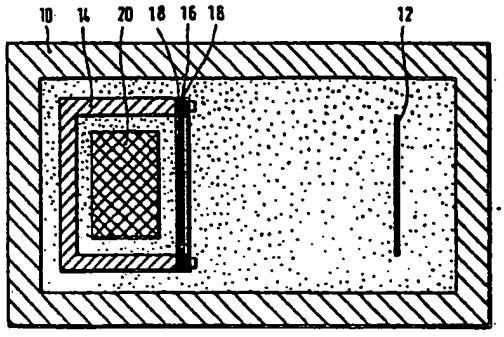
(54) **Method and apparatus for the electro-deposition of lead alloys.**

(57) Apparatus and method for the electro-deposition of a ternary alloy on to a cathode comprises an anolyte containing chamber 14 and a catholyte containing chamber 10 in communication with one another only through the medium of a cation exchange membrane 16. The apparatus is used for depositing a ternary bearing alloy, such as lead-antimony-tin or lead-tin-copper on to the bronze substrate of a steel backed bearing member; the bearing member comprising the cathode 12. Use of the method and apparatus prevents undesirable immersion plating of the lead-containing anode 20 by metals from the plating solution which are more noble than lead.



EP 0 048 579 A1

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Method and Apparatus for the Electro-Deposition of Lead Alloys

This invention relates to a method and apparatus for the electro-deposition of an alloy coating on to a backing member, such a process being of particular interest to the coating of a load carrying bearing surface on to the backing member of a plain bearing.

Such a bearing may comprise for example a half shell backing member of steel with a bronze substrate bonded thereto and on to which is electro-deposited a bearing surface coating of lead-indium or lead-antimony-tin. Binary and ternary alloys can be co-deposited electrolytically as is described for example in British Patents 577335 and 628459 and in U.S.A Patent 2605149. In British Patent 577335 it is stated, and has been verified in tests, that coatings of ternary alloys such as lead-antimony-tin or lead-tin-copper can replace the more usual lead-tin or lead- indium binary alloy coatings as bearing surfaces.

However in the electro-deposition of ternary alloys containing antimony or copper, there is a displacement reaction when a soluble metal anode is used. For example in British Patent 628459 it is stated that antimony will immersion plate on to a lead, lead-tin or lead-tin-antimony anode. In Patent 628459 it is stated that this immersion plating is adherent enough so that the anode may be used two or three times and then the antimony may be scrubbed off and reclaimed and, whereas such a procedure may be acceptable for small scale operation, it would not be feasible to operate a continuous production plating process wherein anodes were required to be removed many times during the working operation for scrubbing.

Similarly if a lead-tin-copper electrolyte is utilised, the copper in the plating solution immersion plates out on to metal anodes such as lead or lead-tin and, although such an electrolyte has been in production use for many years, the removal of all the anodes from the bath during idle periods is required, and frequent additions of copper fluoroborate are necessary to replace losses from the electrolyte.

It is the object of the present invention to provide an improved method and apparatus which will prevent the undesirable immersion plating of a soluble metal anode containing lead by metals from the plating solution which are more noble than lead.

In accordance with one aspect of the invention there is provided apparatus for the electro-deposition of an alloy on to a cathode comprising a first chamber within which the cathode is located and which contains a catholyte solution; a second chamber within which the anode is located and which contains an anolyte solution, and said first and second chambers communicating with one another only through the medium of a cation exchange membrane.

In accordance with a further aspect of the invention there is provided a method of electro-depositing an alloy on to a metal cathode comprising the steps of immersing the cathode in a first chamber containing a catholyte solution; immersing a metal anode in a second chamber containing an anolyte solution communicating with said catholyte solution only through the medium of a cation exchange membrane and applying a direct current between the anode and cathode.

In use of the apparatus and method according to the invention the anolyte will not contain elements capable of immersion plating on to the anode. Thus if the catholyte comprises a lead-antimony-tin plating solution then the anolyte will not contain any antimony. Similarly if the

catholyte comprises a lead-tin-copper plating solution then the anolyte will not contain copper.

When the apparatus is in use, metal ions arising from the anode pass through the cation exchange membrane towards the cathode under the influence of the plating potential. Since the anolyte contains no metal capable of immersion plating on to the anode the anode will remain clean. At the end of a plating operation, when the plating potential is disconnected, the antimony or copper or arsenic in the catholyte (depending on what alloy is being co-deposited) is prevented from entering the anolyte by the physical barrier of the cation exchange membrane. That is to say, metal ions can pass in one direction only, i.e towards the cathode, and then only under the influence of the plating potential applied between the anode and cathode. Thus the anolyte solution in the second chamber remains free of ions capable of immersion plating on to the anode.

A further advantage of the use of a cation exchange membrane to physically separate the catholyte and anolyte solutions is that the composition of the catholyte may be controlled more readily since metal is not lost therefrom by immersion plating which in turn means that the electro-deposited alloys have more consistent compositions.

Other features of the invention will become apparent from the following description given herein solely by way of example and with reference to the accompanying drawing which shows, in diagrammatic form, a plan view of a plating bath in accordance with the invention.

Referring to the drawings there is shown a first chamber 10 within which is locatable a member 12 to be plated and which comprises the cathode; such member may comprise a steel backing member with a bronze substrat bonded thereto and on to which is to be co-deposited a ternary alloy as a

bearing surface. This first chamber 10 is capable of being filled with the catholyte solution.

At the end of the first chamber 10 remote from the cathode 12 there is provided a second chamber 14 wholely contained within the first chamber and communicating therewith only through the medium of a cation exchange membrane 16. This second chamber 14 is conveniently of box like rectangular configuration having an open top and an open front across which is secured the exchange membrane 16 by means of detachable clamping plates and gaskets. To provide support and protection for the exchange membrane 16 a sheet 18 of porous polyethylene may be sealingly located by the gaskets on one or both sides of the membrane 16 the polyethylene sheeting 18 being provided to prevent physical damage to the exchange membrane 16 and also providing support against sag or swelling of the exchange membrane which may occur in use.

The cation exchange membrane is a proprietary item and may be of the type available from Permutit-Boby of Brentford, Middlesex, England.

The anode 20 is locatable within the second chamber 14 and the chamber 14 is capable of being filled with an anolyte solution to at least the same level as that of the catholyte solution in the first chamber 10. It may be preferable for the level of the anolyte solution to be above that of the catholyte solution to provide a slight hydrostatic pressure in favour of the anolyte.

The following examples of use of the apparatus will s rve to illustrate the invention:-

Example 1

The apparatus was used for the electro-deposition of a ternary alloy of lead-antimony-tin to give a coating having a basis of lead and containing between 9.5% and 10.5% by weight of antimony and between 5.5% and 6.5% by weight of tin in the deposited alloy. The anode was a lead-tin anode containing 5% to 25% by weight of tin

The cathode comprised a steel backing member on to which was bonded a bronze substrate. It is preferable to electroplate a base coating of cobalt or nickel on to the bronze substrate thereby to give a better surface for the deposition of the required ternary alloy particularly for the prevention of dispersal of tin into the bronze.

The catholyte solution in the first chamber was as follows:-

Lead	150 grammes/litre added as lead fluoroborate
Antimony	6 grammes/litre added as antimony trifluoride
Tin (stannous)	22 grammes/litre added as tin fluoroborate
Resorcinol	7.5 grammes/litre
Gelatin	0.75 grammes/litre
Free fluoroboric acid	20 grammes/litre

The temperature of the catholyte was maintained at 40°C and a cathode current density of 30 amperes per square foot was utilised for approximately 20 minutes to give a deposited alloy thickness of 25 um.

The second chamber was filled with an anolyte solution of the following composition

Lead	150 grammes/litre added as lead fluoroborate
Tin	22 grammes/litre added as tin fluoroborate
Resorcinol	7.5 grammes/litre
Gelatin	0.75 grammes/litre
Free fluoroboric acid	20 grammes/litre

The temperature of the anolyte solution was maintained at 40°C

Example 2

In this example identical constructions of anode and cathode were utilised as in the preceding example but the electrolyte solutions were chosen to give a ternary alloy deposit on the cathode of lead-tin-copper having a basis of lead and containing between 8% and 12% by weight of tin and between 2% and 3% by weight of copper in the deposited alloy.

A catholyte solution of the following composition was used:-

Lead	100 grammes/litre added as lead fluoroborate
Tin (Stannous)	10 grammes/litre added as tin fluoroborate
Copper	3 grammes/litre added as copper fluoroborate

Resorcinol	5 grammes/litre
Gelatin	0.5 grammes/litre
Free fluoroboric acid	40 grammes/litre

The temperature of the catholyte solution was maintained at 25°C and cathode current density of 20 amperes per square foot was utilised for approximately 20 minutes to give a deposited ternary alloy of 25 um thickness.

The anolyte solution was identical in all respects with the catholyte solution with the exception that no copper fluoroborate was present in the anolyte.

In both examples it was found that the anode remained clean and that the plating elements had been lost from the catholyte to the cathode at a controlled rate.

CLAIMS

1. Apparatus for the electro-deposition of an alloy on to a cathode characterised in that the cathode 12 is located in a first chamber 10 which contains a catholyte solution, an anode 20 is located in a second chamber 14 which contains an anolyte solution, and that the first and second chambers communicate with one another only through the medium of a cation exchange membrane 16.

2. Apparatus as claimed in Claim 1 further characterised in that the second chamber 14 is located within the first chamber 10.

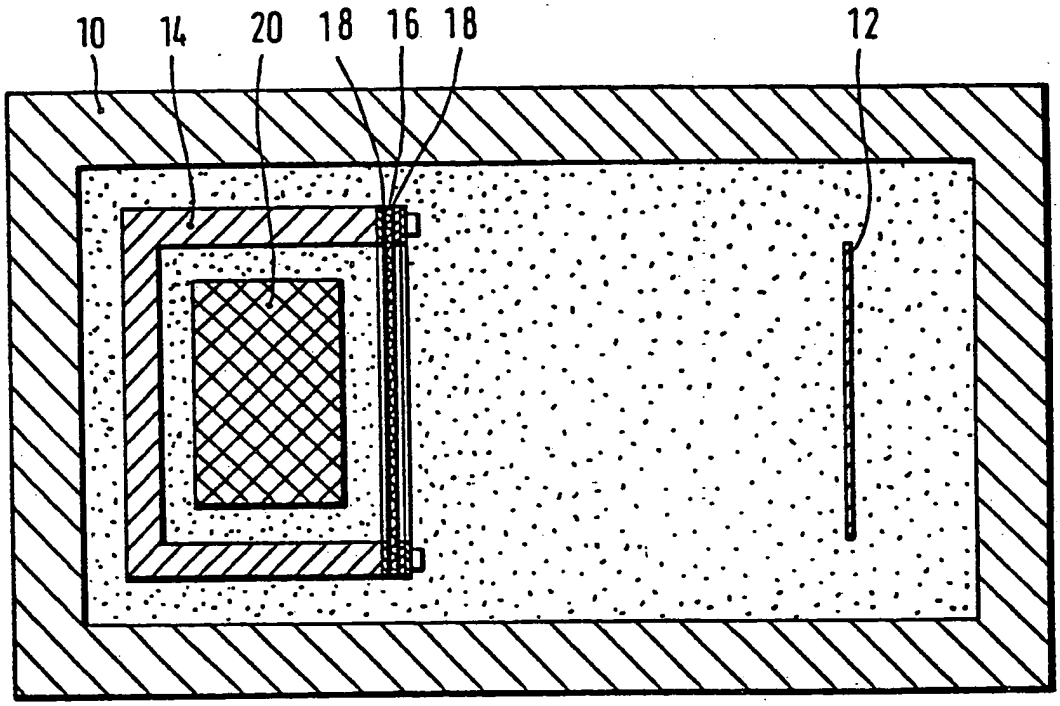
3. Apparatus as claimed in either one of Claims 1 or 2 further characterised in that the anode 20 is a lead-tin anode.

4. Apparatus as claimed in any one of the preceding claims further characterised in that the cathode 12 is a steel backed bearing member.

5. A method of electro-depositing an alloy on to a metal cathode characterised by the steps of immersing the cathode 12 in a first chamber 10 containing a catholyte solution, immersing a metal anode 20 in a second chamber 14 containing an anolyte solution communicating with the catholyte solution only through the medium of a cation exchange membrane 16 and applying a direct current between the anode 20 and cathode 12.

6. A method according to Claim 5 further characterised in that the catholyte solution is a lead-antimony-tin solution, the anolyte solution is a lead-tin solution and the anode 20 is a lead-tin anode.

7. A method according to Claim 5 further characterised in that the catholyte solution is a lead-tin-copper solution, the anolyte solution is a lead-tin solution and the anode 20 is a lead-tin anode.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EUROPEAN SEARCH REPORT

0048579
Application number

EP 81304194.4

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	GB - A - 2 007 713 (DIPSOL CHEMICALS CO LTD) * Example 4 * --	1,3	C 25 D 3/56 C 25 D 17/10 C 25 D 17/02 C 25 C 7/04
	GB - A - 679 947 (A.A. THORNTON) * Claims * --	1,6,7	
D	GB - A - 628 459 (A.A. THORNTON) * Examples; claims * --	1,6	TECHNICAL FIELDS SEARCHED (Int. Cl.³)
D	GB - A - 577 335 (VANDERVELL PRODUCTS LIMITED) * Example; claims * --	1,6	C 25 D C 25 C
	US - A - 3 616 305 (J.P. ARBEZ) * Fig. 2; claims * --	1	
	US - A - 2 793 990 (E. HEYMANN et al.) * Claims * --	1,3,7	
	METAL FINISHING, vol. 74, no. 1, January 1976, METALS AND PLASTICS PUBLICATIONS, INC., Hackensach, N.J. USA pages 30-34 * Page 34, especially "Lead Alloy Deposition" * --	1,6,7	CATEGORY OF CITED DOCUMENTS X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
	US - A - 4 217 198 (I.V. KADIJA et al.) (12-08-1980) * Abstract; claims * ----	1	&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	09-12-1981	SLAMA

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